

Systematic expansion in the order parameter for replica theory of the dynamical glass transition

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It has been shown recently that predictions from Mode-Coupling Theory for the glass transition of hard-spheres become increasingly bad when dimensionality increases, whereas replica theory predicts a correct scaling. Nevertheless if one focuses on the regime around the dynamical transition in three dimensions, Mode-Coupling results are far more convincing than replica theory predictions. It seems thus necessary to reconcile the two theoretic approaches in order to obtain a theory that interpolates between low-dimensional, Mode-Coupling results, and “mean-field” results from replica theory. Even though quantitative results for the dynamical transition issued from replica theory are not accurate in low dimensions, two different approximation schemes –small cage expansion and replicated Hyper-Netted-Chain (RHNC)– provide the correct qualitative picture for the transition, namely a discontinuous jump of a static order parameter from zero to a finite value. The purpose of this work is to develop a systematic expansion around the RHNC result in powers of the static order parameter, and to calculate the first correction in this expansion. Interestingly, this correction involves the static three-body correlations of the liquid, but more importantly, we show that it provides some improvement over the quantitative results of RHNC approximation.

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I. INTRODUCTION

A lot of theoretical activity has been devoted to the general problem of the glass transition in the last decades [1]. Amongst all theories, only two of them emerge from a microscopic description, and without assuming the existence of the glass transition itself. The first theory is an adaptation of the mode-coupling theory of critical dynamics [2] to the glass transition, and was devised by Götze and collaborators [3]. It is nowadays simply denoted by Mode-Coupling Theory (MCT). The other one is the Random-First-Order Transition theory (RFOT) [4], an adaptation to molecular glasses of the mean-field replica theory of spin glasses [5, 6]. While the development of a first principle theory of dynamics is plagued with difficulties (in particular for MCT this is mainly due to its lack of self-consistency) [7–11], replica theory is a static theory, hence calculations are easier, and it has been adapted to the study of the dynamical arrest of structural glasses, *via* three different approximation schemes: the small cage expansion [12, 13], the effective potential approximation [14, 15] and the replicated Hyper-Netted-Chain (RHNC) approximation [16, 17].

The first two are formulated in terms of the local cage size around a particle. This parameter is expected to be infinite in the liquid phase (the particles are free to visit all space) but finite and small in the glass phase, thus can serve as an order parameter for the glass transition. However the large jump of this scalar order parameter (from infinity to small!) seems to prevent one from obtaining good quantitative results around the dynamical glass transition, whereas predictions are more robust deep inside the glass phase [12, 13]. The situation is reversed for the RHNC approximation: the theory is formulated in terms of a two-point order parameter (a pair correlation function between two replicas, equivalent to the non-ergodicity parameter), that displays a jump from zero to a non-zero (but non small) value at the dynamical transition. The RHNC approximation correctly predicts, in a qualitative way, the phenomenology of the dynamical glass transition, i.e. the freezing of density fluctuations due to the appearance of an exponential number of metastable states in the system [16, 17]. However, the neglect of some important corrections (see [15] for a detailed discussion) both prevents to obtain accurate quantitative results near the glass transition, and gives inconsistent results deep inside the glass phase [16]. The main problem is that the structural properties of the glass (and in particular the non-ergodicity parameter) are found to be quantitatively incorrect. For example, the non-ergodicity parameter for hard spheres shown in [15] and in Fig. 1 of this paper poorly compares to the experimental ones found for example in [18].

The difficulties of the replica method in treating the dynamical glass transition, compared to the quantitative success of MCT in the same regime [19], must not hide its successes: it is able, within a purely static framework, and starting from the Hamiltonian of the system, to pre-

dict without assuming it the appearance of a large number of metastable states, to quantify this number through the complexity, and to make predictions for the critical properties of the long-time dynamics [40–42]. It is thus of primary importance to continue developing the RHNC approximation scheme in order to probe the limits of this replica (static) approach, and in order to set the stage for an hypothetical theory that would be able to reconcile dynamic, MCT-like computations, and static, replica computations. Interestingly, a first bridge was made between the two [20] by looking at the dynamics in a replicated liquid, and treating these dynamics in a MCT fashion. Unfortunately, this approach suffers from the same lack of internal self-consistency as the original MCT computation, and it only succeeds in reinforcing the general belief that MCT and replica theory can indeed be unified in a coherent scheme (still neglecting activated events), as was done in the context of spin glasses [21].

In this paper we perform a first step in the general task of making RHNC an efficient quantitative theory of the dynamical transition, by setting up a perturbative expansion in powers of the static order parameter used in replica theory to characterize the glass phase. This order parameter is proportional to the non-ergodicity factor, and our expansion thus corresponds to the “weak glass” expansion sought for in [22]. We calculate the first correction to RHNC in this expansion, and show that it already leads to some improvement of the quantitative results, while the qualitative picture remains stable. Interestingly, we show that this new term, and the subsequent ones, involve the three-body and higher order correlations of the liquid, which currently receive renewed interest: even though two-body static correlations of the liquid are blind to the presence of the glass transition, it is possible that three-body functions are more sensitive to it [23]. Our work paves the way to more powerful re-summations, maybe allowing to unify the three versions of replica theory for structural glasses (small cage, effective potential, and RHNC) in a unique scheme, and possibly obtain a quantitatively competitive theory of the dynamical transition.

The paper is organized as follows. In Section II we briefly review the replica interpretation of the glass transition, focusing on the two main order parameters, static and dynamic, currently used to describe it in a theoretical way. In Section III we introduce the replicated liquid theory that will allow us to perform approximations on the static order parameter, and briefly review its simplest implementation, the replicated Hyper-Netted-Chain approximation [16]. We then explain how to proceed from this approximation to perform an expansion in powers of the static order parameter. In Section IV, the first correction to the replicated Hyper-Netted-Chain approximation is obtained, and shown to involve three-body correlation functions of the liquid. This section is mostly technical and can be safely jumped by the reader uninterested in details of the computation. A numerical solving of this improved Hyper-Netted-Chain approximation is

presented in Section V, and we conclude in Section VII.

II. STATIC ORDER PARAMETER FOR GLASSES

The glass transition is *a priori* defined in a dynamical way as the temperature below which (or density above which) density fluctuations become frozen in the liquid. However, replica computations on mean-field spin glasses have given an insight into the thermodynamics of glasses, and provided us with a static order parameter for the glass transition [6]. In this section we recall the procedure needed to define and calculate this order parameter, and show its relation with the dynamical order parameter traditionally used in glass physics, namely the non-ergodicity parameter.

A. Order parameter with replicas

In order to detect the glass transition from a static observable, one introduces identical copies of the system of interest. Consider an integer number m of copies of the system, i.e. a liquid of $m \times N$ particles. The copies are indexed by alphabetical characters a, b, \dots , and the position of particle i in copy a will be denoted by x_i^a . Within each copy, all the particles interact with a given pair potential, but each particle in a given copy is attracted to all other particles of all other copies via an attractive pair potential of infinitesimal amplitude ε . Consider for example copy a and copy b , with $a \neq b$. In analogy with usual liquid theory (see [24] and Eq. (15) in the following), each of them has a microscopic density defined by:

$$\hat{\rho}_a(x) = \sum_{i=1}^N \delta(x - x_i^a), \quad (1)$$

Consider now the generalization of the pair correlation function, as defined in [24] and Eq. (16) below, to a replicated system:

$$\begin{cases} h_{ab}(x, y) = \frac{\langle \hat{\rho}_a(x) \hat{\rho}_b(y) \rangle}{\rho^2} - 1 \text{ for } a \neq b, \\ h_{aa}(x, y) = \frac{\langle \hat{\rho}_a(x) \hat{\rho}_a(y) \rangle}{\rho^2} - 1 - \frac{1}{\rho} \delta(x - y). \end{cases} \quad (2)$$

Note that, for $a \neq b$, the coincident point term is absent, because particle i of copy a interacts with all particles of copy b , including particle i , whereas within copy a , particle i does not interact with itself.

We want to study what happens in the thermodynamic limit $N \rightarrow \infty$ when the coupling potential strength ε is vanishingly small. As usual, a phase transition will be signaled by the fact that the limits $N \rightarrow \infty$ and $\varepsilon \rightarrow 0$ do not commute [25–27]. More precisely, if we suppose that a dynamical transition occurs at ρ_d , with a mean-field phenomenology, we will have that:

- if $\rho < \rho_d$ and letting ε go to zero, the two copies de-correlate, i.e. $h_{ab} = 0$, and the system is not trapped in a metastable state. In this case the limit $\varepsilon \rightarrow 0$ and $N \rightarrow \infty$ commute.
- if $\rho > \rho_d$, the two copies are trapped into the same metastable state by their mutual attraction ε . Letting ε go to zero after $N \rightarrow \infty$, the two copies will stay correlated and $h_{ab} \neq 0$. Note that obviously the copies will de-correlate if ε is set to zero before $N \rightarrow \infty$, hence the two limits do not commute in the glass phase.

Of course this transition is observed only if metastable states are present in the system, that are able to constrain copies to stay in the same state, in the thermodynamic limit and in the long-time limit. As we will see in the following, this assumption can be checked self-consistently within the theory. In order to recover the equilibrium properties of the original, non-replicated system, one has to make an analytic continuation to non-integer values of m , the number of replicas, and take the limit $m \rightarrow 1$ at the end of the calculations [16, 26].

The general procedure is then the following:

- Compute the equilibrium properties of a m -times replicated liquid, with small attraction ε between different copies
- Take the thermodynamic limit, and compute the desired quantities as functions of m
- Send the attraction ε to zero
- Take the limit $m \rightarrow 1$ to recover the original system

We show in the following that calculating the static order parameter defined above with this prescription amounts to evaluating the non-ergodicity parameter of the glass.

B. Link with the dynamic order parameter

In the mean-field replica interpretation, the partition function of the system is supposed to be separated into many pure states, that correspond to minima of the free-energy. Because of this separation, averages can be separated in two operations: first an average inside a state α , denoted by $\langle \bullet \rangle_\alpha$, and then an average over all states denoted by $\overline{\bullet}$. Calculating $h_{ab}(x, y)_\varepsilon$, the correlation between copy a and b (with $a \neq b$), we take into account that the attractive coupling between a and b will force them into the same state α leading to:

$$h_{ab}(x, y)_\varepsilon = \frac{\langle \hat{\rho}(x) \hat{\rho}(y) \rangle_{\alpha, \varepsilon}}{\rho^2} - 1. \quad (3)$$

Letting the interaction go to zero will allow the two replicas to de-correlate inside the state, leading to:

$$\lim_{\varepsilon \rightarrow 0} h_{ab}(x, y)_\varepsilon = \frac{\langle \hat{\rho}(x) \rangle_\alpha \langle \hat{\rho}(y) \rangle_\alpha}{\rho^2} - 1. \quad (4)$$

Note that the average density inside a state need not be constant, because translational invariance is restored only after summation over all the states.

Independently, the time-dependent density-density correlation that is the focus of MCT, and more generally dynamical calculations, is defined by:

$$F(x, y, t) = \langle (\hat{\rho}(x, t) - \rho)(\hat{\rho}(y, 0) - \rho) \rangle, \quad (5)$$

where at $t = 0$ the system is taken at equilibrium. Note that the initial time value of this function is related to the inverse Fourier transform of the structure factor:

$$F(x, y, 0) = \rho^2 h(x, y) + \delta(x - y)\rho. \quad (6)$$

Above the glass transition, and in the long time limit, the system eventually gets stuck in a metastable state α , and we have:

$$F(x, y, t) \xrightarrow{t \rightarrow \infty} \overline{\langle \hat{\rho}(x) \hat{\rho}(y) \rangle_\alpha} - \rho^2. \quad (7)$$

But the system is at least able to de-correlate inside the state, giving:

$$F(x, y, t) \xrightarrow{t \rightarrow \infty} \overline{\langle \hat{\rho}(x) \rangle_\alpha \langle \hat{\rho}(y) \rangle_\alpha} - \rho^2 = \rho^2 h_{ab}(x, y). \quad (8)$$

Now taking the Fourier transform of equations (6) and (8) we get:

$$\begin{aligned} F(k, t) &\xrightarrow{t \rightarrow \infty} \rho^2 h_{ab}(k), \\ F(k, 0) &= \rho S(k), \end{aligned} \quad (9)$$

where $S(k)$ is the structure factor defined in [24] and Eq. (17) below. Finally the non-ergodicity factor is traditionally defined as:

$$f(k) \equiv \lim_{t \rightarrow \infty} \frac{F(k, t)}{F(k, 0)}, \quad (10)$$

so that we get [15, 20]:

$$f(k) = \frac{\rho h_{ab}(k)}{S(k)} \text{ with } a \neq b. \quad (11)$$

We thus find that, in the replica interpretation, the dynamical and static order parameter are the same physical observable. This parallel is exploited in order to compute long-time properties of the dynamics from replica calculations, for example in [40] or [41, 42].

III. EXPANSION IN POWERS OF THE ORDER PARAMETER

Before trying to obtain a good theory for our replicated system and studying the glass phase, we must introduce the liquid theory tools used to describe the liquid phase, in order to fix notations and for the sake of completeness.

In this paper, we will consider for concreteness a system composed of N spheres of diameter D interacting via a hard-sphere pair potential v :

$$v(x, y) = \begin{cases} \infty & \text{if } |x - y| \leq D, \\ 0 & \text{otherwise.} \end{cases} \quad (12)$$

Note that we use here the hard-sphere potential mainly for the sake of simplicity, because it has only one parameter, the density, and because its liquid properties are well studied, both numerically and theoretically. However the general computation scheme we develop here is not restricted to this potential and can be applied to any pairwise additive potential.

A microscopic configuration σ of the system specifies all the positions x_i of the particles, with $i \in [1, N]$. The Hamiltonian of the system is then $H(\sigma) = \sum_{i < j} v(x_i - x_j)$. For any inverse temperature $\beta = 1/k_B T$, the Boltzmann weight of such a configuration is $e^{-\beta H(\sigma)}$, which can be either 0 if there is any overlap between spheres, or 1 if no spheres overlap. The temperature thus plays no role here. To stay in contact with standard liquid theory notations, we will nonetheless keep it explicit in this subsection. We fix units so that $D = 1$ and $k_B = 1$.

For a given chemical potential μ and an eventual external potential Ψ , the grand canonical partition function of the system is defined as:

$$Z_{\text{liq}} = \text{Tr } e^{-\beta H(\{x_i\}) + \sum_i \nu(x_i)}, \quad (13)$$

where the grand-canonical trace is defined as $\text{Tr } \bullet = \sum_{N=0}^{\infty} \frac{1}{N!} \int \prod_{i=1}^N dx_i \bullet$, and the generalized chemical potential is defined as $\nu(x) = \beta\mu - \beta\Psi(x)$. The grand-canonical average of an observable \mathcal{O} is defined by:

$$\langle \mathcal{O}(\{x_i\}) \rangle_{\text{liq}} \equiv \frac{1}{Z} \text{Tr } \mathcal{O}(\{x_i\}) e^{-\beta H(\{x_i\}) + \sum_i \nu(x_i)}, \quad (14)$$

We define the microscopic density $\hat{\rho}$ and the average density ρ as:

$$\begin{aligned} \hat{\rho}(x) &= \sum_{i=1}^N \delta(x - x_i), \\ \rho(x) &= \langle \hat{\rho}(x) \rangle_{\text{liq}}. \end{aligned} \quad (15)$$

We limit ourselves to translationally invariant systems, so that the average density is constant in the system and $\rho(x) = \rho$ in all points. The pair correlation h is linked to the normalized second cumulant of the microscopic density, apart from a coincident point term:

$$\begin{aligned} h(x, y) &= \frac{1}{\rho^2} \left\langle \sum_{i=1}^N \sum_{j \neq i} \delta(x - x_i) \delta(y - x_j) \right\rangle_{\text{liq}} - 1 \\ &= \frac{\langle \hat{\rho}(x) \hat{\rho}(y) \rangle_{\text{liq}}}{\rho^2} - 1 - \frac{1}{\rho} \delta(x - y). \end{aligned} \quad (16)$$

Subtracting 1 gives a function that decays to zero at large interparticle distance, and thus allows to compute its Fourier transform. In a translational invariant system, $h(x, y)$ depends only on $|x - y|$, and we define the structure factor S , related to its Fourier transform as:

$$S(k) = 1 + \rho h(k) . \quad (17)$$

h is only the second function of a whole hierarchy of cumulants of the microscopic density. In the following we will need the next cumulant in this hierarchy:

$$W_{\text{liq}}^{(3)}(x, y, z) = \langle \hat{\rho}(x) \hat{\rho}(y) \hat{\rho}(z) \rangle + 2\rho(x)\rho(y)\rho(z) - \rho(x) \langle \hat{\rho}(y) \hat{\rho}(z) \rangle - \{2 \text{ permutations} \} . \quad (18)$$

Usual liquid theory approximations start from the Legendre transform of $\ln Z$ with respect to the chemical potential, using the fact that the chemical potential is coupled to the microscopic density. Thus we define:

$$\left\{ \begin{array}{l} \Gamma_{\text{liq}}[\rho] = \int_x \rho(x) \nu^*[\rho](x) - \ln Z_{\text{liq}}[\nu^*[\rho]] , \\ \nu_a^*[\rho] \text{ such that } \left. \frac{\delta \ln Z_{\text{liq}}[\nu]}{\delta \nu_a(x)} \right|_{\nu^*[\rho]} = \rho(x) . \end{array} \right. \quad (19)$$

From the virial expansion [43], one can show that this functional is composed of an ideal gas term Γ_{id} plus an excess term:

$$\begin{aligned} \Gamma_{\text{liq}}[\rho] &\equiv \Gamma_{\text{id}}[\rho] + \Gamma_{\text{ex}}[\rho] , \\ \Gamma_{\text{id}}[\rho] &\equiv \int_x \rho(x) [\ln \rho(x) - 1] . \end{aligned} \quad (20)$$

From this functional, one can define a hierarchy of correlation functions (equivalent to the vertex functionals in field theory) called the direct correlation functions [24]:

$$c_{\text{liq}}^{(n)}(x_1, \dots, x_N) = \frac{\delta^n (\Gamma_{\text{liq}}[\rho] - \Gamma_{\text{id}}[\rho])}{\delta \rho(x_1) \dots \delta \rho(x_N)} . \quad (21)$$

By the properties of the Legendre transform (the calculation is shown formally in Eq. (57) and can be straightforwardly applied to the case of liquid theory), the second order direct correlation function $c_{\text{liq}}^{(2)}$, that will be denoted by c in the following, is the inverse function of h , which is expressed by the Ornstein-Zernike equation:

$$(1 + \rho h(k))(1 - \rho c(k)) = 1 , \quad (22)$$

where $c(k)$ is the Fourier transform of $c_{\text{liq}}^{(2)}(r)$ as defined in Eq. (21). We can rewrite this equation in a more usual field-theoretic notation:

$$\int_z G_{\text{liq}}(x, z) \Gamma_{\text{liq}}^{(2)}(z, y) = \delta(x, y) , \quad (23)$$

where we have defined the propagator $G_{\text{liq}}(x, y) = \rho(x)\delta(x, y) + \rho(x)\rho(y)h(x, y)$ and the two-point vertex

functional of liquid theory $\Gamma_{\text{liq}}^{(2)}(x, y) = \frac{1}{\rho(x)}\delta(x, y) - c(x, y)$. Differentiating this equation with respect to the density we obtain the third order Ornstein-Zernike equation:

$$\begin{aligned} \Gamma_{\text{liq}}^{(3)}(x, y, z) &= \\ &- \int_{x', y', z'} \Gamma_{\text{liq}}^{(2)}(x, x') \Gamma_{\text{liq}}^{(2)}(y, y') \Gamma_{\text{liq}}^{(2)}(z, z') W_{\text{liq}}^{(3)}(x', y', z') , \end{aligned} \quad (24)$$

where $\Gamma_{\text{liq}}^{(3)}$ is related to the third order direct correlation function via Eq. (21):

$$\Gamma_{\text{liq}}^{(3)}(x, y, z) = -\frac{1}{\rho(x)^2} \delta(x, y) \delta(x, z) - c_{\text{liq}}^{(3)}(x, y, z) . \quad (25)$$

We will make repeated use of relations (23–25) in the next section.

A. Replicated liquid theory

We can now formulate in the same way the partition function of our replicated system, defining:

$$Z_m = \text{Tr} e^{-\frac{\beta}{2} \sum'_{i,j,a,b} v_{ab}(x_i^a - x_j^b) + \sum_{i,a} \nu_a(x_i^a)} , \quad (26)$$

where v_{ab} is equal to v for $a = b$, and v_{ab} is a small attractive coupling when $a \neq b$. The prime on the summation sign \sum' means that when $a = b$, the summation must exclude the case $i = j$, and the trace operation is now defined as: $\text{Tr} \bullet = \sum_{N=0}^{\infty} \frac{1}{N!^m} \int \prod_{a=1}^m \prod_{i=1}^N dx_i^a \bullet$. For the sake of simplicity, ν in the following will denote the set of m chemical potentials $\{\nu_a\}_{a=1\dots m}$, and \mathbf{v} will denote the set of m^2 pair potentials $\{v_{ab}\}_{a,b=1\dots m}$. Equivalently the family of m average densities $\{\rho_a\}_{a=1\dots m}$ defined in Eq. (1) will be denoted by ρ and the family of m^2 correlation functions $\{h_{ab}\}_{a,b=1\dots m}$ will be denoted by \mathbf{h} .

As for the non replicated liquid case, one can define the Legendre transform of the free-energy with respect to ν , to obtain an m -dependent Legendre transform $\Gamma_{1,m}$:

$$\left\{ \begin{array}{l} \Gamma_{1,m}[\rho] = \sum_a \int_x \rho_a(x) \nu_a^*[\rho](x) - \ln Z_m[\nu^*] , \\ \left. \frac{\delta \ln Z_m[\nu]}{\delta \nu_a(x)} \right|_{\nu^*} = \rho_a(x) . \end{array} \right. \quad (27)$$

However, our goal here is to focus on the static order parameter h_{ab} defined earlier. It is thus preferable to obtain a theory that explicitly depends on it in order to control approximations in terms of this quantity. The key point is to notice that the pair potentials v_{ab} are coupled to the two-point densities of the liquid $\rho_{ab}^{(2)}$, defined by:

$$\begin{aligned} \hat{\rho}_{ab}^{(2)}(x, y) &= \hat{\rho}_a(x) \hat{\rho}_b(y) - \hat{\rho}_a(x) \delta_{ab} \delta(x, y) , \\ \rho_{ab}^{(2)}(x, y) &= \langle \hat{\rho}_{ab}^{(2)}(x, y) \rangle . \end{aligned} \quad (28)$$

This quantity is trivially related to h_{ab} by $\rho_{ab}^{(2)}(x, y) = \rho_a(x)\rho_b(y)[1 + h_{ab}(x, y)]$, and we define it for convenience. Indeed we remark that:

$$\begin{aligned} \frac{\delta \ln Z_m}{\delta(-\beta v_{ab}(x, y))} &= \frac{1}{2}\rho_{ab}^{(2)}(x, y) , \\ \Rightarrow \frac{\delta \Gamma_{1,m}[\boldsymbol{\rho}, \mathbf{v}]}{\delta \beta v_{ab}(x, y)} &= \frac{1}{2}\rho_{ab}^{(2)}(x, y) . \end{aligned} \quad (29)$$

This relation explains why it will be easier to manipulate the properties of the Legendre transform that we define below in terms of $\rho^{(2)}$ than in terms of h , avoiding unnecessary density factors in the calculations. Also for later convenience, we define the propagator and two-point vertex function:

$$\begin{aligned} G_{ab}(x, y) &= \rho_a(x)\delta_{ab}\delta(x, y) + \rho_a(x)\rho_b(y)h_{ab}(x, y) , \\ \Gamma_{ab}^{(2)}(x, y) &= \frac{1}{\rho_a(x)}\delta_{ab}\delta(x, y) - c_{ab}(x, y) , \end{aligned} \quad (30)$$

where c_{ab} is the generalization to mixtures of the direct correlation function. Again we have the OZ relation, i.e. that $\text{Tr } \Gamma_{ac}^{(2)}(x, z)G_{cb}(z, y) = \delta_{ab}\delta(x, y)$, or equivalently $h_{ab}(x, y) = c_{ab}(x, y) - \sum_c \int_z h_{ac}(x, z)\rho_c(z)c_{cb}(z, y)$.

Defining Γ_m the Legendre transform of $\Gamma_{1,m}$ with respect to $\beta\mathbf{v}$ we get:

$$\left\{ \begin{aligned} \Gamma_m[\boldsymbol{\rho}, \mathbf{h}] &= -\frac{1}{2} \sum_{a,b} \int_{x,y} \rho_{ab}^{(2)}(x, y)\beta v_{ab}^*(x, y) \\ &\quad + \Gamma_{1,m}[\boldsymbol{\rho}, \mathbf{v}^*] , \\ \frac{\delta \Gamma_{1,m}[\boldsymbol{\rho}, \mathbf{v}]}{\delta \beta v_{ab}(x, y)} \Big|_{\mathbf{v}^*} &= \frac{1}{2}\rho_{ab}^{(2)}(x, y) , \end{aligned} \right. \quad (31)$$

where we have written Γ_m as a function of h since $\rho^{(2)}$ and h are simply related.

The functional Γ_m , when evaluated at the true correlation function, coincides with $\Gamma_{1,m}$, but now a stationary principle allows to derive self-consistent equations for the

correlation function, because as a consequence of Legendre transforms properties we have:

$$\begin{aligned} \frac{\delta \Gamma_m[\boldsymbol{\rho}, \mathbf{h}]}{\delta h_{ab}(x, y)} &= \rho_a(x)\rho_b(y) \frac{\delta \Gamma_m[\boldsymbol{\rho}, \mathbf{h}]}{\delta \rho_{ab}^{(2)}(x, y)} \\ &= -\frac{1}{2}\rho_a(x)\rho_b(y)\beta v_{ab}^*[\mathbf{h}](x, y) . \end{aligned} \quad (32)$$

We know that the values v_{ab}^* of the pair potentials that lead to the real correlation function are v_{ab} , so that the real correlation functions h_{ab} are solutions to the self-consistent equation:

$$\frac{\delta \Gamma_m[\boldsymbol{\rho}, \mathbf{h}]}{\delta h_{ab}(x, y)} = -\frac{1}{2}\rho_a(x)\rho_b(y)\beta v_{ab}(x, y) . \quad (33)$$

Now performing an approximation for Γ_m and using Eq. (33) leads to an approximate value of h_{ab} , and evaluating the approximated Γ_m at this value of h_{ab} lead to an approximate free-energy that is consistent with the approximate h_{ab} obtained. Finally, as described in Section II, we set the inter-replica potential to zero, which distinguishes between the case $a = b$, where $v_{ab} = v$, and the case $a \neq b$, where v_{ab} is now set to zero. Note that we set the inter-replica potential to zero only after taking the Legendre transform. This ensures that the thermodynamic limit has been taken, and will give rise to non trivial inter-replica correlations. We look for persisting inter-replica correlations, which will indicate the glass phase [16].

B. Morita & Hiroike functional

Morita & Hiroike [44] showed that the functional Γ_m can be written as:

$$\Gamma_m[\boldsymbol{\rho}, \mathbf{h}] = \Gamma_{Id}[\boldsymbol{\rho}, \mathbf{h}] + \Gamma_{Ring}[\boldsymbol{\rho}, \mathbf{h}] + \Gamma^{2PI}[\boldsymbol{\rho}, \mathbf{h}] , \quad (34)$$

where:

$$\begin{aligned} \Gamma_{Id}[\boldsymbol{\rho}, \mathbf{h}] &= \sum_a \int_x \rho_a(x) [\ln \rho_a(x) - 1] + \frac{1}{2} \sum_{a,b} \int_{x,y} \rho_a(x)\rho_b(y) [(1 + h_{ab}(x, y)) \ln(1 + h_{ab}(x, y)) - h_{ab}(x, y)] , \\ \Gamma_{Ring}[\boldsymbol{\rho}, \mathbf{h}] &= \frac{1}{2} \sum_{n \geq 3} \frac{(-1)^n}{n} \text{Tr } \rho_{a_1}(x_1) h_{a_1 a_2}(x_1, x_2) \cdots \rho_{a_n}(x_n) h_{a_n a_1}(x_n, x_1) , \end{aligned} \quad (35)$$

and $\Gamma_{2PI}[\boldsymbol{\rho}, \mathbf{h}]$ is the sum of all 2PI diagrams, which are usual Mayer diagrams composed of black nodes $\rho_a(x)$ and links $h_{ab}(x, y)$, such that when two links are removed from the diagrams, it does not disconnect in two separate parts. Γ_{Ring} is the sum of all ring diagrams. The Hyper-Netted-Chain (HNC) approximation [45], and other per-

formant approximations of liquid theory start from this exact functional. This result is exactly what we wanted: we have now an explicit functional of our static order parameter. Before turning to the expansion of this quantity in powers of the order parameter, we first review the results obtained within RHNC approximation, starting

from the above Gibbs free-energy, since it is at the core of our expansion.

C. RHNC approximation

RHNC amounts to discard all the 2PI diagrams, giving an analytic expression for the free-energy as a functional of \mathbf{h} which is just the sum of the two terms in Eq. (35). With this approximate functional, that we will denote by Γ_m^{HNC} , we obtain self consistent equations for the h_{ab} by making use of Eq. (33). The sum of ring diagrams, when differentiated with respect to h_{ab} , i.e. when cutting a link, gives a sum of open chains, which is equal to $\mathbf{h} - \mathbf{c}$. Indeed, rewriting the generalization of the Ornstein-Zernike equation (22) to multicomponent mixtures in direct space we have:

$$c_{ab}(x, y) = h_{ab}(x, y) - \sum_c \int_z h_{ac}(x, z) \rho_c(z) c_{cb}(z, y) , \quad (36)$$

which can be solved iteratively with respect to h , to give:

$$c_{ab}(x, y) = h_{ab}(x, y) - \sum_{n=1}^{\infty} (-1)^n h_{aa_1}(x, x_1) \rho_{a_1}(x_1) \cdots \rho_{a_n}(x_n) h_{a_nb}(x_n, y) , \quad (37)$$

where summation over repeated indices and integration over repeated positions has been assumed. Comparison with Eq. (35) shows that $h_{ab} - c_{ab}$ is indeed exactly the derivative of Γ_{Ring} with respect to h_{ab} :

$$\frac{\delta \Gamma_{Ring}[\boldsymbol{\rho}, \mathbf{h}]}{\delta h_{ab}(x, y)} = -\frac{1}{2} \rho_a(x) \rho_b(y) [h_{ab}(x, y) - c_{ab}(x, y)] . \quad (38)$$

Now using the variational principle stated in Eq. (33) along with the prescription described in Section II, we get a set of m^2 self consistent equations:

$$\begin{aligned} \ln(1 + h_{aa}(x, y)) &= -\beta v(x, y) + h_{aa}(x, y) - c_{aa}(x, y) , \\ \ln(1 + h_{ab}(x, y)) &= h_{ab}(x, y) - c_{ab}(x, y) \text{ for } a \neq b . \end{aligned} \quad (39)$$

These equations must be supplemented with the replicated Ornstein-Zernike equations (36) that read in Fourier space:

$$\begin{aligned} c_{aa}(k) &= h_{aa}(k) - \rho h_{aa}(k) c_{aa}(k) - \rho \sum_{b \neq a} h_{ab}(k) c_{ab}(k) , \\ c_{ab}(k) &= h_{ab}(k) - \rho h_{aa}(k) c_{ab}(k) - \rho h_{ab}(k) c_{bb}(k) \\ &\quad - \rho \sum_{c \neq a \neq b} h_{ac}(k) c_{cb}(k) . \end{aligned} \quad (40)$$

In order to follow the prescription of Section II, we must make the free energy analytic in m , then take the limit

$m \rightarrow 1$. In order to do that, we will assume replica symmetry, i.e. that:

$$\begin{cases} h_{aa}(x, y) = h(x, y) & \forall a , \\ h_{ab}(x, y) = \tilde{h}(x, y) & \forall a \neq b . \end{cases} \quad (41)$$

This allows to perform the summations over replica indices in Eqs.(39-40) and perform the $m \rightarrow 1$ limit, to obtain two sets of equations. In the first set, we see that the functions h and c decouple from \tilde{h} and \tilde{c} to give the usual liquid theory HNC approximation and Ornstein-Zernike equation:

$$\begin{cases} \ln(1 + h(x, y)) = -\beta v(x, y) + h(x, y) - c(x, y) , \\ c(k) = h(k) - \rho h(k) c(k) . \end{cases} \quad (42)$$

The second set of equations specify the functions \tilde{h} and \tilde{c} , given h and c :

$$\begin{cases} \ln(1 + \tilde{h}(x, y)) = \tilde{h}(x, y) - \tilde{c}(x, y) , \\ \tilde{c}(k) = \tilde{h}(k) - \rho h(k) \tilde{c}(k) - \rho \tilde{h}(k) c(k) + \rho \tilde{h}(k) \tilde{c}(k) . \end{cases} \quad (43)$$

We can rewrite the second of these equations as:

$$\tilde{c}(k) = \frac{(1 - \rho c(k)) \tilde{h}(k)}{1 + \rho h(k) - \rho \tilde{h}(k)} , \quad (44)$$

and use the definition of the structure factor Eq. (17), the Ornstein-Zernike equation Eq. (22) and the link between h_{ab} for $a \neq b$ with the non-ergodicity factor Eq. (11) to obtain:

$$\tilde{c}(k) = \frac{1}{\rho S(k)} \frac{f(k)}{1 - f(k)} . \quad (45)$$

Since \tilde{c} and \tilde{h} are both related to f , we see that Eq. (43) is a self-consistent equation on the non-ergodicity parameter, which reads

$$\frac{1}{\rho S(k)} \frac{f(k)}{1 - f(k)} = \mathcal{F}[\tilde{h} - \ln(1 + \tilde{h})](k) , \quad (46)$$

where \mathcal{F} denotes a Fourier transform and \tilde{h} is expressed in terms of f by Eq. (11). If we were to make an expansion of the r.h.s. of this equation in powers of $f(k)$ (hence of \tilde{h}), we would get, at lowest order:

$$\frac{f(k)}{1 - f(k)} = \frac{S(k)}{2\rho} \int_q S(q) S(k - q) f(q) f(k - q) . \quad (47)$$

This form of self consistent equation is very reminiscent of the Mode-Coupling result that read [28]:

$$\begin{aligned}
\frac{f(k)}{1-f(k)} &= \frac{S(k)}{2\rho} \int_q \mathcal{M}_{\text{MC}}(k, q) S(q) S(k-q) f(q) f(k-q) , \\
\mathcal{M}_{\text{MC}}(k, q) &= \frac{\rho^2}{k^4} \left(k \cdot qc(q) + k \cdot (k-q)c(k-q) + \rho k^2 c_{liq}^{(3)}(k, -q) \right)^2 \\
&= \left(\frac{k \cdot q}{k^2} [1 - \rho c(q)] + \frac{k \cdot (k-q)}{k^2} [1 - \rho c(k-q)] - \left[1 + \rho^2 c_{liq}^{(3)}(k, -q) \right] \right)^2 \\
&= \left(\frac{k \cdot q}{k^2} \rho \Gamma_{liq}^{(2)}(q) + \frac{k \cdot (k-q)}{k^2} \rho \Gamma_{liq}^{(2)}(k-q) + \rho^2 \Gamma_{liq}^{(3)}(k, -q) \right)^2 .
\end{aligned} \tag{48}$$

Note here the presence of the three-body direct correlation function of the liquid, even though it is usually neglected, since it has been shown to be negligible with respect to the other, two-body term [29], except for special cases [30]. However the RHNC result if expanded at this order in h_{ab} is trivial (in the sense that the kernel $\mathcal{M} = 1$), and reminiscent of the result obtained by [9] by a dynamical field-theory calculation. Whether this is a coincidence or not is an open question at this stage. Nevertheless, we performed this expansion of the logarithmic term in Eq. (43) only to show the striking similarities that exist between replica calculations and usual Mode-Coupling ones.

If we do not perform this truncation, and solve the RHNC approximation Eq. (43) combined with the HNC approximation for the liquid part Eq. (42), we already find, *without assuming it*, the existence of a dynamical transition [16]: for hard spheres, for densities lower than $\varphi_d \approx 0.599$ (where the packing fraction $\varphi = \rho\pi/6$), the solution to Eq. (43) is always $h_{ab} = 0$, i.e. a liquid phase, whereas h_{ab} discontinuously jumps to a non zero value for $\varphi \geq \varphi_d$, indicating the glass transition. This results is quite good, because the dynamical transition for three-dimensional hard spheres is estimated to be around $\varphi_d \approx 0.57$. Note that Mode-Coupling Theory instead strongly underestimates the transition [19]. We show in Fig. 1 the resulting non-ergodicity factor [15] for a packing fraction $\varphi = 0.6$, obtained by solving the set of equations (43). This is the crucial problem of RHNC: $f(k)$ is quite far from the numerical results (see [18, 19]) which are instead well captured by the Mode-Coupling theory.

The goal of this paper is to demonstrate that the order parameter h_{ab} with $a \neq b$ can be used as an organizing device for the theory in order to gradually incorporate higher-order correlations of the liquid into the replica result. Of course, we see in Fig. 1 that the order parameter is not a small quantity, and thus an expansion in powers of h_{ab} is not *a priori* justified. Note however that RHNC already re-sums an infinite number of diagrams containing arbitrary numbers of h_{ab} links, which maybe explains its ability to predict a transition towards a non-small value of the order parameter. Our purpose here is to build from RHNC and incorporate more diagrams, and we will see that even keeping the lowest order correction

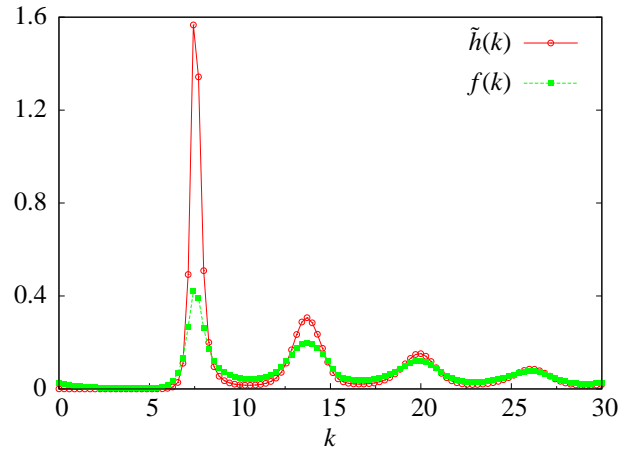


FIG. 1: Filled squares: Non-ergodicity factor of hard spheres at packing fraction 0.599670 (i.e. at the transition), obtained from the replicated Hyper-Netted-Chain approximation Eq. (43), combined with the liquid theory HNC approximation Eq. (42). Open circles: the corresponding order parameter $\tilde{h}(k)$

already provides some improvement over RHNC.

D. Improvements over the liquid quantities

Before turning to the study of the expansion in powers of the order parameter, a remark is in order. We have seen that in the $m = 1$ limit, the liquid quantities decouple from the inter-replica correlations: Eq. (42) is in fact independent from the off-diagonal correlations. This allows us to use any liquid theory approximation to evaluate liquid quantities that appear in our equations. Formally, this is justified by writing the Gibbs free-energy Γ in Eq. (34) as:

$$\Gamma_m[\rho, \mathbf{h}] = \Gamma_m^{\text{HNC}}[\rho, \mathbf{h}] + \Gamma_{liq}^{2PI}[\rho, \mathbf{h}] + \Gamma_{glass}^{2PI}[\rho, \mathbf{h}] , \tag{49}$$

where Γ_{liq}^{2PI} is the sum of all 2PI diagrams that do not contain any h_{ab} , $a \neq b$ links. We can now use the variational principles, which will give the full liquid correlation function for the $a = b$ components. For a given approximation of Γ_{glass}^{2PI} , we will obtain a self consistent equation

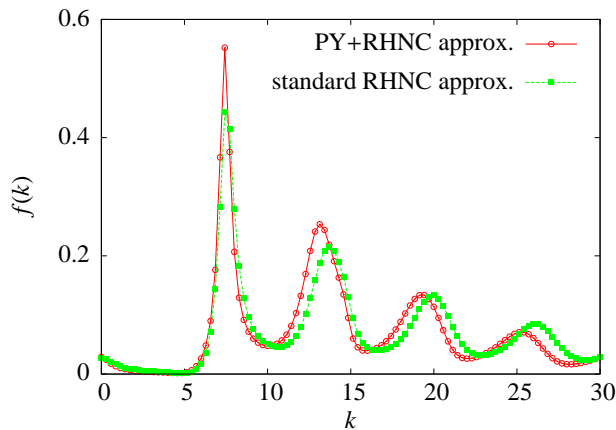


FIG. 2: Non-ergodicity factor as a function of the wave vector at packing fraction 0.6, for the standard replicated HNC calculation, and from the combination of PY approximation for the diagonal part and RHNC for the off-diagonal correlation.

for the $a \neq b$ components. Neglecting altogether Γ_{glass}^{2PI} , we recover the set of equations Eqs.(43), in which c and h are now the full liquid correlation functions. Of course, inside the glass phase, the liquid quantities cannot be obtained numerically or experimentally, so that such a full re-summation is useless. Instead, we need to have an approximation that can be extrapolated from the liquid phase. For example we can choose the PY approximation for the liquid quantities. Choosing to work at a packing fraction (defined as $\varphi = \pi\rho/6$) $\varphi = 0.6$, which is ex-

pected to be above the dynamical transition, we solved the RHNC equation for the off-diagonal part, Eq. (43) with the PY direct correlation function as an input for the diagonal part, and found that this brings about a little improvement over standard RHNC results. It is known that the PY approximation gives a less important underestimation of the peak of $S(k)$, which is the main ingredient that leads to the glass transition. In standard RHNC as in the PY version of it, we find a transition from a liquid state at $\varphi < \varphi_d$ to a glass state at $\varphi \geq \varphi_d$, where the self-consistent equation on \tilde{h} admits a non-zero solution. The value of the critical density is shifted downwards from $\varphi_c \approx 0.599$ to 0.591 by the use of PY approximation, which is an improvement, even if modest. We show the resulting non-ergodicity factor in the two sets of approximations in Fig. 2. Even though use of the PY approximation gives a slightly larger non ergodicity factor, the result is still very small when compared to simulation and experimental data, where f is much closer to 1 at small wave vectors. We conclude that the source of the problem in the static approach is not the diagonal part of the liquid. We should therefore seek for a way of improving the equation for the off-diagonal correlation, Eq. (43).

E. Systematic expansion in powers of \tilde{h}

To go further than the replicated Hyper-Netted-Chain approximation, we perform an expansion of Γ_{glass}^{2PI} in powers of \tilde{h} :

$$\Gamma_{glass}^{2PI}[\rho, \mathbf{h}] = \sum_{n=1}^{\infty} \text{Tr} \left[\frac{1}{n!} \frac{\delta^n \Gamma_{glass}^{2PI}[\rho, \mathbf{h}]}{\delta h_{a_1 b_1}(x_1, y_1) \cdots \delta h_{a_n b_n}(x_n, y_n)} h_{a_1 b_1}(x_1, y_1) \cdots h_{a_n b_n}(x_n, y_n) \right], \quad (50)$$

where $a_i \neq b_i \forall i$, and we have underlined the fact that the zeroth order term is absent since the full functional must vanish in the liquid phase, where $\Gamma_{glass}^{2PI} = 0$ by construction.

Now consider the “glassy” 2PI diagrams in Eq. (49). We can show that these diagrams must contain at least three \tilde{h} lines: this idea was already used in the “weak glass” expansion of [22, Appendix A3]. Indeed, a \tilde{h} link joins two nodes that have different replica indices, say a and b . All the nodes connected to the a node by a path of h links must also have replica index a , and the same applies for the b node. Thus all \tilde{h} links are nodal links: they separate the diagram in two parts, each of it has a different replica index. If a 2PI diagram would contain one or two \tilde{h} links, then differentiating once or twice with respect to \tilde{h} would cut the diagram in two, which is in contradiction with the fact that the diagram is 2PI. Thus we proved that all 2PI diagrams contain either zero or

three or more \tilde{h} links. Moreover, a diagram that contains three \tilde{h} links can have at most six parts composed of h links and ρ nodes that all have the same replica index. A little reflexion shows that the only possibility to construct such diagram and make it 2PI is the one pictured in Fig.3.

From this analysis, we showed that the non HNC terms in the free-energy Eq. (34) can be organized as a series in powers of \tilde{h} , the first term of which are $\mathcal{O}(\tilde{h}^3)$. This last observation is crucial, since it will allow us to make the computation tractable.

In the following we will need to distinguish the derivatives with respect to the density and with respect to the correlation functions, as well as derivatives with respect to chemical potentials and with respect to pair potentials.

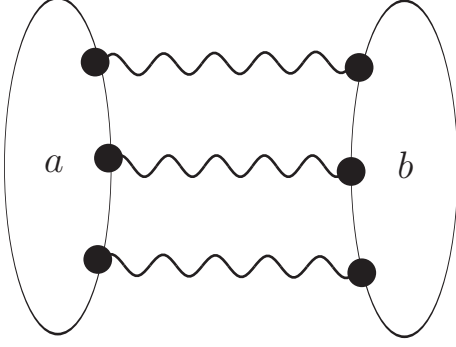


FIG. 3: Diagrams that contribute to the free-energy at order \tilde{h}^3 . A wiggly line joining two replica indices a and b is a h_{ab} , with $a \neq b$ function, a black dot attached to a zone with replica index a is an integration point weighted by a density factor ρ_a .

We define:

$$\begin{aligned}\Gamma_a^{(1,0)}(x_1) &= \frac{\delta \Gamma_m[\boldsymbol{\rho}, \mathbf{h}]}{\delta \rho_a(x_1)}, \\ \Gamma_{ab}^{(0,1)}(x_1, y_1) &= \frac{\delta \Gamma_m[\boldsymbol{\rho}, \mathbf{h}]}{\delta h_{ab}(x_1, y_1)}, \\ \Gamma_{a,cd}^{(1,1)}(x_1; x_2, y_2) &= \frac{\delta^2 \Gamma_m[\boldsymbol{\rho}, \mathbf{h}]}{\delta \rho_a(x_1) \delta h_{cd}(x_2, y_2)},\end{aligned}\quad (51)$$

and so on. We will also need to define derivatives of $\ln Z_m$ with respect to the chemical potentials and pair potentials:

$$\begin{aligned}W_a^{(1,0)}(x_1) &= \left. \frac{\delta \ln Z_m[\boldsymbol{\nu}, \mathbf{v}]}{\delta \nu_a(x_1)} \right|_{\boldsymbol{\nu}^*, \mathbf{v}^*}, \\ W_{ab}^{(0,1)}(x_1, y_1) &= \left. \frac{\delta \ln Z_m[\boldsymbol{\nu}, \mathbf{v}]}{\delta (-\beta v_{ab}(x_1, y_1))} \right|_{\boldsymbol{\nu}^*, \mathbf{v}^*}, \\ W_{a,cd}^{(1,1)}(x_1; x_2, y_2) &= \left. \frac{\delta^2 \ln Z_m[\boldsymbol{\nu}, \mathbf{v}]}{\delta \nu_a(x_1) \delta (-\beta v_{cd}(x_2, y_2))} \right|_{\boldsymbol{\nu}^*, \mathbf{v}^*},\end{aligned}\quad (52)$$

and so on. Because of our analysis, we see that the $n = 1$ and $n = 2$ terms in Eq. (50) are necessary zero. In the following, we will calculate the first non-zero term in this expansion, the third-order term. In practice, we found it easier to calculate the third derivative of the total free energy, and subtract from it the third order term of the RHNC free-energy, i.e. we calculated, with the above notations:

$$\begin{aligned}\Gamma_{ab,cd,ef}^{(0,3)}(x_1, y_1; x_2, y_2; x_3, y_3) &= \\ \frac{\delta^3 \left[\Gamma_m^{HNC}[\boldsymbol{\rho}, \mathbf{h}] + \Gamma_{glass}^{2PI}[\boldsymbol{\rho}, \mathbf{h}] \right]}{\delta h_{ab}(x_1, y_1) \delta h_{cd}(x_2, y_2) \delta h_{ef}(x_3, y_3)},\end{aligned}\quad (53)$$

with $a \neq b$, $c \neq d$ and $e \neq f$. The third order term of the RHNC free-energy will be simply calculated from Eqs.(34-35).

IV. TREATMENT AT THIRD ORDER IN THE ORDER PARAMETER

In order to make progress, we must find a way to evaluate the third derivative of the free-energy with respect to the correlation function. We can make use of the properties of the Legendre transform to do so. The only difficulty is that we performed two Legendre transformations, with respect to different objects, which renders difficult the use of properties such as the one written in Eq. (24).

A. Third-order Ornstein-Zernicke relation

Considering, for simplicity, a discretized version of our theory, we have that $\boldsymbol{\rho}$ is a m by M matrix, where M is the number of points of the underlying lattice, and \mathbf{h} is a m by m by M by M object, and the same applies to $\boldsymbol{\nu}$ and \mathbf{v} . We can write the two pairs $\boldsymbol{\rho}, \boldsymbol{\rho}^{(2)}$ and $\boldsymbol{\nu}, \mathbf{v}$ in two (big) vectors:

$$\begin{aligned}\Psi &\equiv \left(\boldsymbol{\rho}, \frac{1}{2} \boldsymbol{\rho}^{(2)} \right), \\ \Phi &\equiv (\boldsymbol{\nu}, -\beta \mathbf{v}),\end{aligned}\quad (54)$$

with the convention that if $i > mM$ an index i of the vector Ψ or Φ must be understood as a group of two spatial coordinates (x_i, y_i) and two replica indices (a_i, b_i) , but if $i \leq mM$, it must be understood as one spatial coordinate and one replica index. The double Legendre transform Γ_m can then be written as:

$$\begin{cases} \Gamma_m[\Psi] = \text{Tr } \Phi^* \Psi - \ln Z_m[\Phi^*], \\ \text{with } \Phi^* \text{ such that } \left. \frac{\delta \ln Z_m[\Phi]}{\delta \Phi} \right|_{\Phi^*} = \Psi. \end{cases}\quad (55)$$

We have by definition of the Legendre transform:

$$\Phi_1^* = \frac{\delta \Gamma_m[\Psi]}{\delta \Psi_1}. \quad (56)$$

We can perform a functional derivative of this equation with respect to Ψ_2 to get:

$$\begin{aligned}\left(\left. \frac{\delta^2 \ln Z_m[\Phi]}{\delta \Phi_1 \delta \Phi_2} \right|_{\Phi^*} \right)^{-1} &= \frac{\delta^2 \Gamma_m[\Psi]}{\delta \Psi_1 \delta \Psi_2}, \\ \Leftrightarrow \delta_{12} &= \text{Tr} \left(\frac{\delta^2 \Gamma_m[\Psi]}{\delta \Psi_1 \delta \Psi_4} \frac{\delta^2 \ln Z_m[\Phi]}{\delta \Phi_4 \delta \Phi_2} \right|_{\Phi^*} \right).\end{aligned}\quad (57)$$

Computing a third derivative with respect to Ψ_3 , we get formally:

$$\begin{aligned}0 &= \text{Tr} \left(\frac{\delta^3 \Gamma_m[\Psi]}{\delta \Psi_1 \delta \Psi_3 \delta \Psi_4} \frac{\delta^2 \ln Z_m[\Phi]}{\delta \Phi_2 \delta \Phi_4} \right|_{\Phi^*} \right) \\ &+ \text{Tr} \left(\frac{\delta^2 \Gamma_m[\Psi]}{\delta \Psi_1 \delta \Psi_4} \frac{\delta^2 \Gamma_m[\Psi]}{\delta \Psi_4 \delta \Psi_5} \frac{\delta^3 \ln Z_m[\Phi]}{\delta \Phi_2 \delta \Phi_4 \delta \Phi_5} \right|_{\Phi^*} \right),\end{aligned}\quad (58)$$

And multiplying through by a second derivative of Γ_m and using Eq. (57), we get:

$$\frac{\delta^3 \Gamma_m[\Psi]}{\delta \Psi_1 \delta \Psi_2 \delta \Psi_3} = - \text{Tr} \left(\frac{\delta^2 \Gamma_m[\Psi]}{\delta \Psi_1 \delta \Psi_1'} \frac{\delta^2 \Gamma_m[\Psi]}{\delta \Psi_2 \delta \Psi_2'} \frac{\delta^2 \Gamma_m[\Psi]}{\delta \Psi_3 \delta \Psi_3'} \frac{\delta^3 \ln Z_m[\Phi]}{\delta \Phi_1' \delta \Phi_2' \delta \Phi_3'} \Big|_{\Phi^*} \right), \quad (59)$$

This is a standard equation that can be found in any textbook on field theory, for example in [31], that expresses

the relation between vertex functions and propagators of the theory. It coincides with Eq. (24) if the vectors Ψ and Φ contain only the first mM components.

We are interested in the continuum space limit of this expression, evaluated in the liquid, and with 1, 2 and 3 that are all greater than mM . With explicit spatial coordinates and replica indices and implicit summation and integration over repeated indices and variables, and after replacing derivatives with respect to $\rho^{(2)}$ with derivatives with respect to h , we get:

$$\begin{aligned} \Gamma_{ab,cd,ef}^{(0,3)}(x_1, y_1; x_2, y_2; x_3, y_3) &= - \frac{8}{\rho^6} \Gamma_{ab,a'}^{(1,1)}(x_1, y_1; x'_1) \Gamma_{cd,c'}^{(1,1)}(x_2, y_2; x'_2) \Gamma_{ef,e'}^{(1,1)}(x_3, y_3; x'_3) W_{a',c',e'}^{(3,0)}(x'_1, x'_2, x'_3) \\ &- \frac{16}{\rho^8} \Gamma_{ab,a'b'}^{(0,2)}(x_1, y_1; x'_2, x'_3) \Gamma_{cd,c'}^{(1,1)}(x_2, y_2; x'_2) \Gamma_{ef,e'}^{(1,1)}(x_3, y_3; x'_3) W_{a'b',c',e'}^{(2,1)}(x'_1, y'_1; x'_2, x'_3) \\ &- \text{two permutations } \{(a, b); (x_1, y_1)\} \leftrightarrow \{(c, d); (x_2, y_2)\} \leftrightarrow \{(e, f); (x_3, y_3)\} \\ &- \frac{32}{\rho^{10}} \Gamma_{ab,a'}^{(1,1)}(x_1, y_1; x'_1) \Gamma_{cd,c'd'}^{(0,2)}(x_2, y_2; x'_2, y'_2) \Gamma_{ef,e'f'}^{(0,2)}(x_3, y_3; x'_3, y'_3) W_{a',c'd',e'f'}^{(1,2)}(x'_1; x'_2, y'_2; x'_3, y'_3) \\ &- \text{two permutations } \{(a, b); (x_1, y_1)\} \leftrightarrow \{(c, d); (x_2, y_2)\} \leftrightarrow \{(e, f); (x_3, y_3)\} \\ &- \frac{64}{\rho^{12}} \Gamma_{ab,a'b'}^{(0,2)}(x_1, y_1; x'_1, y'_1) \Gamma_{cd,c'd'}^{(0,2)}(x_2, y_2; x'_2, y'_2) \Gamma_{ef,e'f'}^{(0,2)}(x_3, y_3; x'_3, y'_3) W_{a'b',c'd',e'f'}^{(0,3)}(x'_1, y'_1; x'_2, y'_2; x'_3, y'_3). \end{aligned} \quad (60)$$

There are two types of objects that we need to compute in order to use this relation: cumulants of the microscopic densities that are generated by the differentiation of $\ln Z_m$ with respect to ν_a and ν_{ab} , and second derivatives of Γ_m with respect to ρ_a and h_{ab} . In the end, we want to evaluate these objects in the liquid phase where \tilde{h} is equal to zero. But we know that the free energy can be written as the HNC free energy plus 2PI contributions, that are $\mathcal{O}(\tilde{h}^3)$, i.e. contain more than three \tilde{h} links. Thus when taking one or two derivatives of the 2PI diagrams with respect to \tilde{h} , they still will contain at least one \tilde{h} link, and will all cancel out when evaluated at zero \tilde{h} . This proves that Eq. (60) when evaluated in the liquid phase can be computed by replacing the Γ_m functionals in the r.h.s. by Γ_m^{HNC} .

Thus the needed derivatives of Γ_m can be computed starting from Eq. (34) by dropping the 2PI diagrams. The only difficult term is the sum of ring diagrams. Its first derivative is given in Eq. (38). This equation can be rewritten with the propagators and vertex functions G and $\Gamma^{(2)}$, and can then be easily differentiated with respect to h by noting that, since they are inverse from each other, we must have:

$$\Gamma^{(2)} = \frac{1}{G} \Rightarrow \frac{\delta \Gamma^{(2)}}{\delta G} = -\frac{1}{G^2} = -\Gamma^{(2)} \Gamma^{(2)}. \quad (61)$$

Explicitly, we obtain:

$$\begin{aligned} \frac{\delta \Gamma_{ab}^{(2)}(x_1, y_1)}{\delta G_{cd}(x_2, y_2)} &= -\Gamma_{ab}^{(2)}(x_1, y_1) \Gamma_{cd}^{(2)}(x_2, y_2), \\ \Rightarrow \frac{\delta c_{ab}(x_1, y_1)}{\delta h_{cd}(x_2, y_2)} &= \left(\frac{1}{\rho_a(x_1)} \delta_{ab} \delta(x_1, y_1) - c_{ab}(x_1, y_1) \right) \\ &\quad \times \left(\frac{1}{\rho_c(x_2)} \delta_{cd} \delta(x_2, y_2) - c_{cd}(x_2, y_2) \right). \end{aligned} \quad (62)$$

One can also obtain this result by a diagrammatical analysis, since c is written as a sum of chains of h bonds. We thus obtain:

$$\Gamma_{a,cd}^{(1,1)}(x_1; x_2, y_2) |_{liq} = -\frac{1}{2} \rho (\delta_{ac} \delta(x_1, x_2) + \delta_{ad} \delta(x_1, y_2)), \quad (63)$$

$$\begin{aligned} \Gamma_{ab,cd}^{(0,2)}(x_1, y_1; x_2, y_2) |_{liq} &= \frac{1}{2} \rho^4 \delta_{ac} \delta_{bd} \Gamma_{liq}^{(2)}(x_1, x_2) \Gamma_{liq}^{(2)}(y_1, y_2) \\ &\equiv \frac{1}{2} \rho^4 \delta_{ac} \delta_{bd} \Gamma_{HNC}^{(0,2)}(x_1, x_2; y_1, y_2). \end{aligned} \quad (64)$$

We see that these derivatives are delta functions for what concerns the replica indexes. If we drop the space indexes, we can thus already perform trace over replica

indexes in Eq. (60), to get: to obtain:

$$\begin{aligned} \Gamma_{ab,cd,ef}^{(0,3)} &= \frac{1}{\rho^3} W_{a,c,e}^{(3,0)} \\ &\quad - \frac{2}{\rho^2} \Gamma_{HNC}^{(0,2)} \otimes W_{ab,c,e}^{(2,1)} - \{\text{two perms.}\} \\ &\quad + \frac{4}{\rho} \Gamma_{HNC}^{(0,2)} \otimes \Gamma_{HNC}^{(0,2)} \otimes W_{a,cd,ef}^{(1,2)} + \{\text{two perms.}\} \\ &\quad - 8 \Gamma_{HNC}^{(0,2)} \otimes \Gamma_{HNC}^{(0,2)} \otimes \Gamma_{HNC}^{(0,2)} \otimes W_{ab,cd,ef}^{(0,3)}, \end{aligned} \quad (65)$$

where \otimes means space convolution with respect to two spatial indexes.

Finally, we only have left the task to compute the derivatives of the logarithm of the partition function (the terms $W^{(0,3)}$, $W^{(1,2)}$, ...). These terms, equivalently to the one written in Eq. (18) for the liquid, are averages of microscopic one or two-point densities, that are easily computed within the 1RSB framework that we use here, as we explain in the following.

B. 1RSB structure of the theory

We denote by $\langle \bullet \rangle$ the equilibrium average for the replicated system. Once again, in the limit $v_{ab}(r) \rightarrow 0$, all replicas fall in the same state but are otherwise uncorrelated inside the state. Finally, we want to evaluate all our averages in the liquid phase. This leads to the following rule to compute the average $\langle \bullet \rangle$: one should

- factorize the averages $\langle \bullet \rangle$ when they involve different replicas, and

- remove the replica indexes.

- replace $\langle \bullet \rangle = \langle \bullet \rangle_{liq}$

For instance, for any spatial argument, and for $a \neq b$, we have that following the prescription above

$$\langle \hat{\rho}_a \hat{\rho}_b \rangle = \langle \hat{\rho}_a \rangle \langle \hat{\rho}_b \rangle = \langle \hat{\rho} \rangle_{liq} \langle \hat{\rho} \rangle_{liq} = \rho^2. \quad (66)$$

Similarly, assuming that different letters denote different values of the indexes:

$$\langle \hat{\rho}_a \hat{\rho}_a \hat{\rho}_b \rangle = \langle \hat{\rho}_a \hat{\rho}_a \rangle \langle \hat{\rho}_b \rangle = \langle \hat{\rho} \hat{\rho} \rangle_{liq} \langle \hat{\rho} \rangle_{liq} = \rho(G_{liq} + \rho^2). \quad (67)$$

$$\begin{aligned} \langle \hat{\rho}_{ab}^{(2)} \hat{\rho}_{ac}^{(2)} \rangle &= \langle \hat{\rho}_a \hat{\rho}_b \hat{\rho}_a \hat{\rho}_c \rangle = \langle \hat{\rho}_a \hat{\rho}_a \rangle \langle \hat{\rho}_b \rangle \langle \hat{\rho}_c \rangle \\ &= \langle \hat{\rho} \rangle_{liq} \langle \hat{\rho} \rangle_{liq} \langle \hat{\rho} \hat{\rho} \rangle_{liq} \\ &= \rho^2 (G_{liq} + \rho^2). \end{aligned} \quad (68)$$

We will thus obtain quantities that do not depend on replica indices anymore, allowing to sum over these indices, and finally take the $m \rightarrow 1$ limit. The free-energy will have an overall factor $m(m-1)$, and thus we will consider the free energy divided by $m(m-1)$. All the terms that are $\mathcal{O}((m-1)^2)$ or higher-order in $m-1$ will thus disappear in the limit $m \rightarrow 1$. This will eliminate a large number of terms in the complicated expression (60). Indeed, recalling that we will calculate a free-energy correction of the form:

$$\begin{aligned} \delta \Gamma_m[\rho, \mathbf{h}] &= \frac{1}{3!} \sum_{a \neq b} \sum_{c \neq d} \sum_{e \neq f} \int_{x_1, y_1, \dots, x_3, y_3} \Gamma_{ab,cd,ef}^{(0,3)}(x_1, y_1; x_2, y_2; x_3, y_3) h_{ab}(x_1, y_1) h_{cd}(x_2, y_2) h_{ef}(x_3, y_3) \\ &= \frac{1}{3!} \sum_{a \neq b} \sum_{c \neq d} \sum_{e \neq f} \int_{x_1, y_1, \dots, x_3, y_3} \Gamma_{ab,cd,ef}^{(0,3)}(x_1, y_1; x_2, y_2; x_3, y_3) \tilde{h}(x_1, y_1) \tilde{h}(x_2, y_2) \tilde{h}(x_3, y_3). \end{aligned} \quad (69)$$

we see that the trace over replica indexes will let appear m (for example the number of ways to choose the index a) and $m-1$ factors (the number of ways to choose $b \neq a$, once a has been chosen). If the terms in $\Gamma^{(0,3)}$ did not depend on replica indexes at all, we would obtain a factor $(m-1)^3$ from the three summations over replica indexes b , d , and f , and the contribution would cancel out in the $m \rightarrow 1$ limit. In the different terms of Eq. (65), we see that the first two lines contain quantities that do not depend on two or three indexes. These terms will give contributions that are at least $\mathcal{O}((m-1)^2)$, and thus will cancel out in the $m \rightarrow 1$ limit. Another remark allows

to discard also the terms coming from the third line of Eq. (65): each time a replica indexes structure for $W^{(1,2)}$ is chosen, it is easy to see that this structure always have at least a multiplicity $m(m-1)$, thus making these terms $\mathcal{O}((m-1)^2)$ also.

Finally we are left with only the last line of Eq. (65) to compute, which amounts to compute $W^{(0,3)}$, under the prescription described in the beginning of this subsection.

C. Final calculation

Before turning to the explicit evaluation of $W^{(0,3)}$, it is useful to remark that, within the 1RSB structure that we have, we can parametrize the replica dependance of our quantities in a simple way.

Take a matrix that depends on two pairs of replica indexes $M_{ab,cd}$, with $a \neq b$ and $c \neq d$ (we do not explicit the space indexes). Examination of the different possibilities for a, b, c and d shows that we have only three genuinely different possibilities:

$$M_{ab,cd} = \begin{cases} M_{ab,ab} , \\ M_{ab,ac} , \\ M_{ab,cd} . \end{cases} \quad (70)$$

This is a consequence both of the 1RSB ansatz and of the symmetry of the functions with respect to permutations of indexes (and their associated space indexes). This can be summarized in:

$$M_{ab,cd} = M_1 \frac{\delta_{ac}\delta_{bd} + \delta_{ad}\delta_{bc}}{2} + M_2 \frac{\delta_{ac} + \delta_{ad} + \delta_{bc} + \delta_{bd}}{4} + M_3 , \quad (71)$$

where M_1, M_2 and M_3 are related to the above terms by:

$$\begin{cases} M_1 = 2 [M_{ab,ab} - 2M_{ab,ac} + M_{ab,cd}] , \\ M_2 = 4 [M_{ab,ac} - M_{ab,cd}] , \\ M_3 = M_{ab,cd} . \end{cases} \quad (72)$$

The quantity that we are interested in is a matrix that depends on three pairs of indexes. In this case there are 8 topologically different possibilities [32]:

$$W_{ab,cd,ef}^{(0,3)} = \begin{cases} W_1 = W_{ab,ab,ab} , \\ W_2 = W_{ab,bc,ca} , \\ W_3 = W_{ab,ab,ac} , \\ W_4 = W_{ab,ab,cd} , \\ W_5 = W_{ab,ac,ad} , \\ W_6 = W_{ab,ac,bd} , \\ W_7 = W_{ab,ac,de} , \\ W_8 = W_{ab,cd,ef} . \end{cases} \quad (73)$$

A relation like Eq. (71) is again possible, but cumbersome, and we do not write it explicitly because we do not need it. By using the prescription for calculating averages of one and two-point densities described above, we can easily compute the W_i . We obtain:

$$W_1(x_1, \dots, y_3) = \frac{1}{8} \left[\begin{aligned} & W_{liq}^{(3)}(x_1, x_2, x_3) W_{liq}^{(3)}(y_1, y_2, y_3) \\ & + \rho W_{liq}^{(3)}(x_1, x_2, x_3) (\rho^2 + G_{liq}(y_1, y_2) + G_{liq}(y_1, y_3) + G_{liq}(y_2, y_3)) \\ & + \rho W_{liq}^{(3)}(y_1, y_2, y_3) (\rho^2 + G_{liq}(x_1, x_2) + G_{liq}(x_1, x_3) + G_{liq}(x_2, x_3)) \\ & + \rho^2 (G_{liq}(x_1, x_2) G_{liq}(y_1, y_3) + G_{liq}(x_1, x_2) G_{liq}(y_2, y_3) + G_{liq}(x_1, x_3) G_{liq}(y_1, y_2)) \\ & + \rho^2 (G_{liq}(x_1, x_3) G_{liq}(y_2, y_3) + G_{liq}(x_2, x_3) G_{liq}(y_1, y_2) + G_{liq}(x_2, x_3) G_{liq}(y_1, y_3)) \end{aligned} \right] , \quad (74)$$

$$\begin{aligned} W_2(x_1, \dots, y_3) &= \frac{1}{8} \left[\begin{aligned} & G_{liq}(x_1, x_2) G_{liq}(y_1, x_3) G_{liq}(y_2, y_3) \\ & + \rho^2 (G_{liq}(x_1, x_2) G_{liq}(y_1, x_3) + G_{liq}(x_1, x_2) G_{liq}(y_2, y_3) + G_{liq}(y_1, x_3) G_{liq}(y_2, y_3)) \end{aligned} \right] , \\ W_3(x_1, \dots, y_3) &= \frac{1}{8} \left[\rho^3 W_{liq}^{(3)}(x_1, x_2, x_3) + \rho G_{liq}(y_1, y_2) \left(W^{(3)}(x_1, x_2, x_3) + \rho G_{liq}(x_1, x_3) + \rho G_{liq}(x_2, x_3) \right) \right] , \\ W_4(x_1, \dots, y_3) &= \frac{1}{8} \rho^2 G_{liq}(x_1, x_2) G_{liq}(y_1, x_3) , \\ W_5(x_1, \dots, y_3) &= \frac{1}{8} \rho^3 W_{liq}^{(3)}(x_1, x_2, x_3) , \end{aligned} \quad (75)$$

and we find $W_6 = W_7 = W_8 = 0$. The factors $1/8$ come from the fact that a derivative of $\ln Z_m$ with respect to $-\beta v$ gives $\rho^{(2)}/2$ and not $\rho^{(2)}$. Of course, the choice of spatial indexes is arbitrary, and one can make any permutation, as long as it respects the symmetry of the functions. We can now perform the trace over replica

indexes, which will give, apart from the multiplicity of each of the W_i , additional factors due to the $m \rightarrow 1$ limit: a term which has a factor $m-2$ will have an extra -1 factor, a term that has a factor $(m-2)(m-3)$ will

have an extra factor 2, etc.. We obtain:

$$\begin{aligned} \lim_{m \rightarrow 1} \frac{1}{m(m-1)} \sum_{a \neq b} \sum_{c \neq d} \sum_{e \neq f} W_{ab,cd,ef}^{(0,3)} \\ = 4W_1 - 8W_2 - 24W_3 + 16W_4 + 16W_5 \quad (76) \\ = \frac{1}{2} \left[\begin{array}{c} W_{liq}^{(3)}(x_1, x_2, x_3) W_{liq}^{(3)}(y_1, y_2, y_3) \\ - 2G_{liq}(x_1, x_2) G_{liq}(y_1, x_3) G_{liq}(y_2, y_3) \end{array} \right] . \end{aligned}$$

Finally we can perform the convolution with the derivatives of the HNC free energy in Eq. (65), and by making repeated use of the second- and third-order OZ equations we obtain:

$$\begin{aligned} \delta\Gamma_m[\rho, \mathbf{h}] \\ = -\frac{\rho^6}{6} \int_{x_1, \dots, y_3} V(x_1, \dots, y_3) \tilde{h}(x_1, y_1) \tilde{h}(x_2, y_2) \tilde{h}(x_3, y_3) , \end{aligned}$$

$$\begin{aligned} \frac{\Gamma_m[\rho, \mathbf{h}]}{m(m-1)} \Big|_{m=1} = \frac{\Gamma_m^{HNC}[\rho, \mathbf{h}]}{m(m-1)} \Big|_{m=1} - \frac{\rho^6}{12} \int_{x_1, \dots, y_3} c^{(3)}(x_1, x_2, x_3) c^{(3)}(y_1, y_2, y_3) \tilde{h}(x_1, y_1) \tilde{h}(x_2, y_2) \tilde{h}(x_3, y_3) \\ - \frac{\rho^4}{6} \int_{x_1, x_2, x_3, y} c^{(3)}(x_1, x_2, x_3) \tilde{h}(x_1, y) \tilde{h}(x_2, y) \tilde{h}(x_3, y) . \quad (79) \end{aligned}$$

This is the desired result: the next order term in the order-parameter expansion beyond the RHNC approximation. From this approximation of the free-energy, we can make use of the variational principle Eq. (33) to obtain a closed equation on \tilde{h} :

$$\begin{aligned} \tilde{c}(r) = \tilde{h}(r) - \ln[1 + \tilde{h}(r)] \\ + \frac{\rho^4}{2} \int_{r_1 \dots r_4} c_{liq}^{(3)}(r, r_1, r_3) c^{(3)}(0, r_2, r_4) \tilde{h}(r_1, r_2) \tilde{h}(r_3, r_4) \\ + \frac{\rho^2}{2} \int_{r_1, r_2} c^{(3)}(r, r_1, r_2) \tilde{h}(r_1) \tilde{h}(r_2) \\ + \frac{\rho^2}{2} \int_{r_1, r_2} c^{(3)}(0, r_1, r_2) \tilde{h}(r - r_1) \tilde{h}(r - r_2) . \quad (80) \end{aligned}$$

which provides the first correction to Eq. (43). Using translational invariance as well as the invariance under permutation of the three variables of $c^{(3)}$, we get:

$$\begin{aligned} c^{(3)}(r_1, r_2, r_3) = c^{(3)}(r_1 - r_2; r_1 - r_3) \equiv c^{(3)}(r; s) , \\ \text{with } r = r_1 - r_2 \quad s = r_1 - r_3 , \quad (81) \\ c^{(3)}(r; s) = c^{(3)}(s, r) = c^{(3)}(-r; s - r) . \end{aligned}$$

Defining the double fourier transform of $c^{(3)}$ as:

$$c^{(3)}(k, q) = \int_{r, s} e^{-ikr} e^{-iqs} c^{(3)}(r, s) , \quad (82)$$

we obtain two invariance principles:

$$c^{(3)}(k, q) = c^{(3)}(q, k) = c^{(3)}(-k - q, q) . \quad (83)$$

$$\begin{aligned} V(x_1, \dots, y_3) = \frac{1}{2} \Gamma_{liq}^{(3)}(x_1, x_2, x_3) \Gamma_{liq}^{(3)}(y_1, y_2, y_3) \\ - \Gamma_{liq}^{(2)}(x_1, x_2) \Gamma_{liq}^{(2)}(y_1, x_3) \Gamma_{liq}^{(2)}(y_2, y_3) . \quad (77) \end{aligned}$$

This third order correction includes the RHNC term, which reads (here V is the system's volume):

$$-\frac{\rho^2 V}{12} \int_r \tilde{h}(r)^3 + \frac{\rho^3 V}{6} \int_q \frac{\tilde{h}(q)^3}{(1 + \rho h(q))^3} . \quad (78)$$

Subtracting it from the result in Eq. (77), we obtain finally:

Performing a Fourier transformation on our equation we get

$$\begin{aligned} \tilde{c}(k) = \mathcal{F} \left(\tilde{h} - \ln[1 + \tilde{h}] \right) (k) \\ + \frac{\rho^4}{2} \int_q c^{(3)}(-k, q) c^{(3)}(k, -q) \tilde{h}(q) \tilde{h}(k - q) \\ + \frac{\rho^2}{2} \int_q c^{(3)}(q, k - q) \tilde{h}(q) \tilde{h}(k - q) \\ + \frac{\rho^2}{2} \int_q c^{(3)}(-q, -k + q) \tilde{h}(q) \tilde{h}(k - q) , \quad (84) \end{aligned}$$

which using the invariances in Eq. (83) is simplified to:

$$\begin{aligned} \tilde{c}(k) = \mathcal{F} \left(\tilde{h} - \ln[1 + \tilde{h}] \right) (k) \\ + \frac{1}{2} \int_q \left(\left[1 + \rho^2 c^{(3)}(q, k - q) \right]^2 - 1 \right) \tilde{h}(q) \tilde{h}(k - q) . \quad (85) \end{aligned}$$

Before turning to a numerical resolution of this equation, we can again make the naive expansion of the HNC term in powers of \tilde{h} , and keep only the lowest order term, to obtain:

$$\frac{f(k)}{1 - f(k)} = \frac{S(k)}{2\rho} \int_q \rho^4 \Gamma_{liq}^{(3)}(k, -q)^2 S(q) S(k - q) f(q) f(k - q) . \quad (86)$$

This recovers exactly the three-body term in the MCT kernel Eq. (48).

V. THREE-BODY CORRELATIONS AND NUMERICAL SOLVING

We thus have obtained a closed equation of the order-parameter, that necessitates as an input the two- and three-body direct correlation functions of the liquid. We already quoted that we decided here to work within the PY approximation for the two-point functions. It is known [24] that the PY approximation [39], which amounts to treat the fluid in a mean-field approximation, but under the exact constraint that the pair correlation function should vanish for distances smaller than 1 [46], is particularly efficient for hard spheres. Furthermore, we dispose of an analytic expression for the two-body direct correlation function in that approximation [37, 38]. However, the three-body direct correlation function still needs to be approximated. Computing the third-order direct correlation function is in itself a hard problem of liquid theory. The best approximation available was shown by numerical works [34] to be the HNC3 approximation developed by Attard [33]. However, this approximation is very computationally demanding, and because our purpose here is merely to demonstrate the importance of higher-order terms in the expansion in powers of the order parameter, we do not aim at quantitative efficiency, and wish to find a simpler approximation scheme.

A. Denton & Ashcroft approximation

A good compromise between simplicity and efficiency for evaluating the third-order direct correlation function [35] is the Denton-Ashcroft approximation [36]. This approximation gives an analytic form that necessitates as

an input only the second-order direct correlation function, for which we can use the PY result. Within their approximation, $c^{(3)}$ is given by:

$$c_{DA}^{(3)}(k, q) = \frac{1}{c^{(2)}(0)} \left[c^{(2)}(k) \partial_\rho c^{(2)}(q) + c^{(2)}(q) \partial_\rho c^{(2)}(k) \right] - \frac{\partial_\rho c^{(2)}(0)}{(c^{(2)}(0))^2} c^{(2)}(k) c^{(2)}(q) . \quad (87)$$

Within this approximation, angular dependance is neglected. We can recover it by symmetrizing the expression:

$$c_{DAS}^{(3)}(k, q) = \frac{1}{3} \left[c_{DA}^{(3)}(k, q) + c_{DA}^{(3)}(k, |k+q|) + c_{DA}^{(3)}(q, |k+q|) \right] . \quad (88)$$

As stated before, we use as an input the Percus-Yevick direct correlation function, that reads (in units of the hard-sphere diameter):

$$c_{PY}^{(2)}(r) = \begin{cases} -a - 6\varphi br - \frac{1}{2}\varphi ar^3 & r \leq 1 , \\ 0 & r > 1 . \end{cases} \quad (89)$$

where φ is the packing fraction defined by $\varphi = \pi\rho/6$, $a = (1 + 2\varphi)^2/(1 - \varphi)^4$ and $b = -(1 + \varphi/2)^2/(1 - \varphi)^4$. The corresponding Fourier transforms, and derivatives with respect to density are simply computed analytically. Using this approximation for $c^{(3)}$, and writing the integrals in bipolar coordinates by using the isotropy of the liquid, we obtain the following set of equations:

$$\begin{cases} \tilde{c}(k) = F(k) + H(k) , \\ F(r) = \tilde{h}(r) - \ln(1 + \tilde{h}(r)) , \\ H(k) = \frac{\rho S(k)}{8\pi^2 k} \int_0^\infty du \int_{|k-u|}^{k+u} dv u v \tilde{h}(u) \tilde{h}(v) \left(\left[1 + \rho^2 \tilde{c}_{DAS}^{(3)}(u, v; k) \right]^2 - 1 \right) , \end{cases} \quad (90)$$

where we have defined

$$\hat{c}_{DAS}^{(3)}(u, v; k) = \frac{1}{3} \left[c_{DA}^{(3)}(k, u) + c_{DA}^{(3)}(k, v) + c_{DA}^{(3)}(u, v) \right] . \quad (91)$$

Equations (87) – (91) now completely specify our approximation. We present in the following a preliminary numerical resolution in order to demonstrate the importance of the correction H .

B. Numerical resolution methodology

The usual calculation for HNC alone is more stable if we write the iteration procedure in terms of \tilde{c} and $\tilde{\chi} = \tilde{h} - \tilde{c}$, which would give in our case:

$$\tilde{c}(r) = e^{\tilde{\chi}(r) + H(r)} - 1 - \tilde{\chi}(r) , \quad (92)$$

or the same equation with $H = 0$ in the case of RHNC. We first solve the RHNC equation Eq. (90) with $H = 0$, by using PY approximation for the two-point functions.

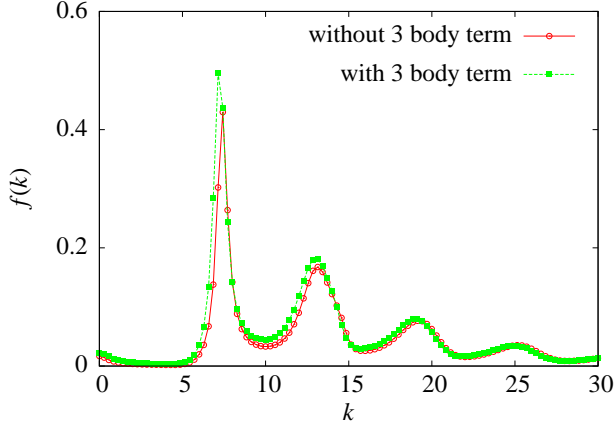


FIG. 4: Non-ergodicity factor as a function of the wave vector very close to the critical point $\varphi = \varphi_d$, for the PY + HNC calculation, and with inclusion of the three body term.

Once a stable solution of the RHNC equations has been found we introduce the three-body correction H , and solve by the very same Picard iterative scheme that is used for solving HNC and RHNC. Explicitly, the resolution will give:

- Start from the value of $k\tilde{c}(k)$, obtained with the previous iteration, or from the old HNC value if first iteration
- Use Eq. (40) to deduce the value of $k\tilde{h}(k)$ and $k\tilde{\chi}(k)$
- Use $k\tilde{h}(k)$ to evaluate $kH(k)$
- Inverse Fourier transform $k\tilde{\chi}(k)$ and $kH(k)$ to obtain $r\tilde{\chi}(r)$ and $rH(r)$
- Use it to evaluate the new $r\tilde{c}(r)$ with Eq. (92)
- Fourier transform $r\tilde{c}(r)$ to obtain $k\tilde{c}(k)$
- Mix it with the old $k\tilde{c}(k)$ to avoid rapid changes
- Repeat these steps until $k\tilde{c}(k)$ has converged

We used a grid of 2^{10} equally spaced points on a box of size 11, and a mixing parameter 0.01. We note that evaluation of the correcting term H in Eq. (90) has a computational cost of order of the square number of points on the grid, significantly slowing down the resolution of the equation, since to avoid instabilities, \tilde{c} is made to evolve very slowly by the mixing procedure.

C. Results and discussion

We solved our improved equation (90) for several packing fractions starting from $\varphi = 0.6$, and decreasing it until the non-trivial solution for \tilde{h} disappeared. We found that the inclusion of the three-body terms, even when using a crude approximation such as the symmetrized Denton & Ashcroft approximation, leads to a strong shift of

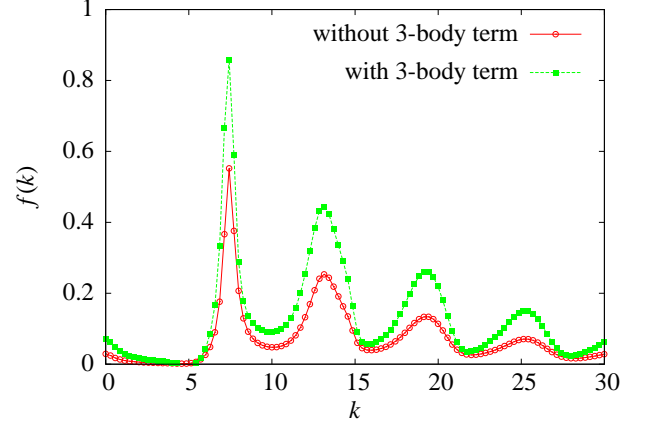


FIG. 5: Non-ergodicity factor as a function of the wave vector at fixed packing fraction 0.6, for the PY + RHNC calculation, and with inclusion of the three body term.

the dynamical transition point from $\varphi_d = 0.591897$ to $\varphi_d = 0.555860$, which is closer to the predicted MCT transition but farther from the numerically estimated transition. It is hard to guess what would be the evolution of φ_d when additional corrections are added.

The resulting non-ergodicity factors at the transition are depicted in Fig. 4. The inclusion of the three body term has significantly enhanced the first peak of $f(k)$ upon inclusion of our correction. These preliminary results must be treated with caution, because it was found [42] that the numerical solving of the RHNC equation is sensitive to the discretization used, and very large grids with a very large number of points must be used in order to obtain stable results. This situation is expected to be the same with the presence of the 3 body term, but the $\mathcal{O}(N^2)$ scaling of the numerical resolution in our case prevented us from performing a stability analysis. The qualitative picture is nevertheless not expected to be modified by these considerations.

In Fig. 5 we show the results inside the glass phase, at a fixed packing fraction $\varphi = 0.6$, with and without inclusion of the three-body term. In this case the effect of including the 3-body term is much bigger and goes in the right direction of increasing $f(k)$ at small k (although still not enough at very small k below the first peak).

VI. HIGHER ORDERS

Our calculation provides the *exact* free-energy and correlation function at order \tilde{h}^2 . This feature allows us to put into correspondence the MCT kernel, which is also $\mathcal{O}(f^2)$, with the replica result. We have seen that the MCT kernel in Eq. (48) contains exactly the three-body contribution we obtain with replica theory, which is already a quite surprising result, given the differences that exist between the two approaches. However, it shows that the two-body terms contained in the MCT kernel are thus impossible to obtain within a static framework. The pe-

cular wave-vector dependance of these terms arise from the calculation of forces, inherent in dynamical theories, but absent in static ones. One could however wonder whether these two-body terms could arise in a dynamical calculation because of the factorization of a dynamical four-point vertex function, that would be forced to be expressed as a $\mathcal{O}(f^2)$ function. Indeed, the main approximation involved in Mode-Coupling theories is the factorization of a four-point function, and since MCT breaks down at high dimensions, it is possible that in the process, “glassy” correlations are factorized along with “liquid” ones, forcefully introducing these new $\mathcal{O}(f^2)$ terms. This is nevertheless highly speculative, and no satisfying dynamical theory exists yet, that would be able to investigate these considerations.

An interesting feature of our calculation is that, once the theory is set up, we can already uncover the next terms with a diagrammatical visualization of the expansion. To go further, we can now wonder what is the term $\mathcal{O}(\tilde{h}^4)$ in the free-energy (that would correspond to a $\mathcal{O}(f^3)$ term for the correlation function). The requirement that we must have 2PI diagrams is quite strong, and it is easy to convince one-self that the only possible diagram that we can construct is shown in Figure 6. The four-point functions that are connected by \tilde{h} lines are made of 1PI diagrams, and we will thus obtain a new contribution to the free-energy that contains the 4-point vertex functions of the liquid:

$$\text{const} \times \int_{r_1, \dots, r_8} \Gamma_{liq}^{(4)}(r_1, \dots, r_7) \Gamma_{liq}^{(4)}(r_2, \dots, r_8) \times \tilde{h}(r_1, r_2) \cdots \tilde{h}(r_7, r_8) . \quad (93)$$

Interestingly, we don’t even have to work out the precise diagrammatics behind this procedure, since RHNC gives a contribution in every diagram, and at all orders in \tilde{h} , so that we can use RHNC to fix the prefactor of each diagram we compute.

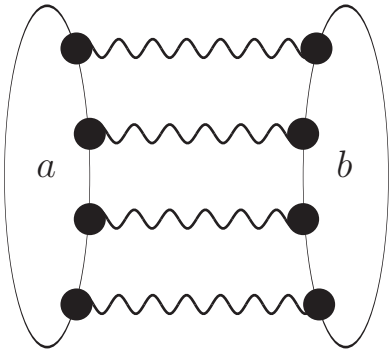


FIG. 6: Diagrams that contribute to the free-energy at order \tilde{h}^4 . A wiggly line joining two replica indices a and b is a h_{ab} , with $a \neq b$ function, a black dot attached to a zone with replica index a is an integration point weighted by a density factor ρ_a .

Computing the n -th order direct correlation function is

still a difficult problem, but with approximations such as the Denton-Ashcroft approximation, that are issued from density functional theory, we can deduce from the approximation for $c^{(3)}$ the corresponding approximation for $c^{(n)}$ by successive differentiation with respect to density. The last difficulty is that an $\mathcal{O}(f^n)$ kernel will require the numerical evaluation of an n -dimensional integral, that have a computational cost of order $\mathcal{O}(N^n)$.

In order to visualize the increasing difficulty of going to the next orders, we show in Figure 7 the possible diagrams at order \tilde{h}^5 . We see that new, intricate terms arise, and that in general, the $\mathcal{O}(\tilde{h}^n)$ contribution will contain all vertex functions of the liquid of orders ranging from 3 to n .

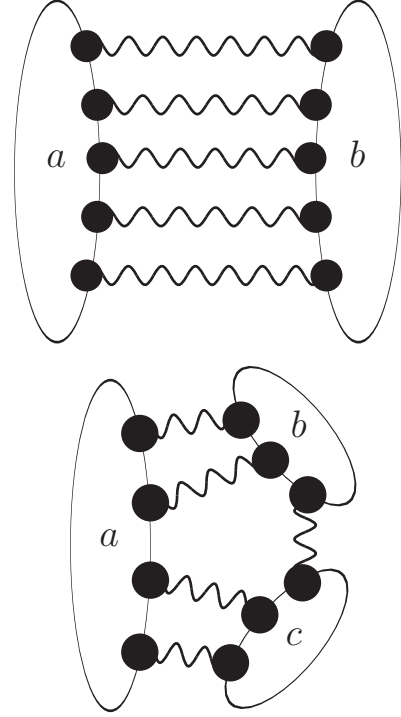


FIG. 7: Diagrams that contribute to the free-energy at order \tilde{h}^5 . A wiggly line joining two replica indices a and b is a h_{ab} , with $a \neq b$ function, a black dot attached to a zone with replica index a is an integration point weighted by a density factor ρ_a .

VII. CONCLUSION AND DISCUSSION

Our analysis shows that the 2PI corrections to the RHNC free energy are quantitatively relevant at the dynamical transition, and must be properly taken into account in order to obtain an accurate static description of the transition. It seems then that only by doing this properly we will be able to make a clear connection between dynamical and static theories of the dynamical transition of glasses. In this respect our results are the following:

- At the level of the RHNC approximation, the equation for $f(k)$ can be developed in powers of $f(k)$. The result is Eq. (47), which corresponds to the Mode-Coupling equation with a kernel equal to 1. The latter is also the result of a zero-th order field theory calculation as reported in [9].
- The first correction to the RHNC approximation provides an additional contribution to the kernel which happens to correspond exactly to the three-body term of the Mode-Coupling kernel.
- The next corrections will give terms proportional to f^3 in the right hand side of Eq. (47), hence no additional contributions to the Mode-Coupling kernel can be generated by these terms. We are forced to conclude that there is no way of generating the terms of the Mode-Coupling kernel proportional to $c(k)$ by means of a static computation.
- We have shown the way to compute higher-order terms, although we expect the numerical resolution of the corresponding approximations to be hard.

It would be therefore very important to perform a similar calculation (namely, a systematic expansion in powers of $f(k)$) also on the dynamical side. This would allow for a systematic comparison of the results. One would then obtain a proper theory for the ergodicity breaking that occurs at ρ_d , free of the ambiguities of MCT, and systematically improvable. Work has been done in this direction in the last years [9, 11, 47, 48], but the situation is still unsatisfactory.

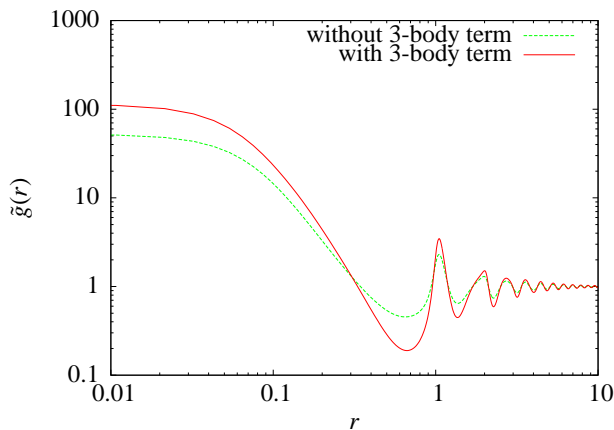


FIG. 8: Inter-replica pair correlation function $\tilde{g}(r)$ at packing fraction $\varphi = 0.6$, with and without three-body correction.

On the static side, the first task to be performed is to reconcile the small cage expansion and the 2PI approach that we use in this work in order to have a unified static theory. The way to do this is indicated by the shape of the pair correlation function between two different replicas at the transition, depicted in Fig. 8. We see that \tilde{g} develops a strong peak at $r = 0$, that dominates the rest of its features. This peak simply reflects the fact that, in the glass phase, two replicas tend to be very close from each other. In the small cage expansion, this idea is reflected in the introduction of a cage size parameter A , which serves as a expansion parameter. In our case a direct introduction of the cage size A would be more difficult, because it would amount to parametrize the pair correlation function by the cage size, which is difficult to do without specifying a given shape of cages. In the high dimensional limit, the cage can safely be approximated by a Gaussian as far as the free energy is concerned [49], but this is not expected to hold in our low dimensional case [50].

It is interesting to note that we have observed, as in Fig. 8 that the inclusion of the three-body term systematically increases the spatial separation between the first, glassy, peak of $\tilde{g}(r)$ and the subsequent, liquid peaks. A clear separation between these contributions allows for an unambiguous definition of the molecules introduced in order to perform small-cage expansions [13, 15], and is clearly a sign that reconciling RHNC with small-cage expansions may not be out of reach.

The large contribution coming from the peak at $r = 0$ in \tilde{g} shows that the diagrams that contribute the most to the free-energy are the most connected ones [15]. It should be possible to put these diagrams in correspondence with the diagrams re-summed in the small cage expansions of [13] and [15] in order to make progress.

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[1] L. Berthier and G. Biroli, *Rev. Mod. Phys.* **83**, 587 (2011)
[2] P. C. Hohenberg and B. I. Halperin, *Rev. Mod. Phys.* **49**, 435 (1977)
[3] W. Götze and L. Sjögren, *Rep. Prog. Phys.* **55**, 241 (1992)

[4] *Structural Glasses and Supercooled Liquids: Theory, Experiment, and Applications*, John Wiley & Sons, Hoboken, New Jersey (2012)
[5] K. Binder and A. P. Young, *Rev. Mod. Phys.* **58**, 801 (1986)

- [6] M. Mézard, G. Parisi, and M. A. Virasoro, *Spin glass theory and beyond*, World Scientific, Singapore (1987)
- [7] D. R. Reichman and P. Charbonneau, J. Stat. Mech. (2005) P05013
- [8] M. E. Cates and S. Ramaswamy, Phys. Rev. Lett. **96**, 135701 (2006)
- [9] A. Andreanov, G. Biroli, and A. Lefèvre, J. Stat. Mech. 2006, P07008
- [10] J.-P. Bouchaud, The mode-coupling theory of supercooled liquids: Does it wear any clothes?, <http://www.condmatjournalclub.org/?p=1022> (2010).
- [11] H. Jacquin and F. van Wijland, Phys. Rev. Lett. **106**, 210602 (2011)
- [12] M. Mézard and G. Parisi, J. Chem. Phys. **111**, 1076 (1999)
- [13] M. Mézard and G. Parisi, Phys. Rev. Lett. **82**, 747 (1999)
- [14] G. Parisi and F. Zamponi, J. Chem. Phys. **123**, 144501 (2005)
- [15] G. Parisi and F. Zamponi, Rev. Mod. Phys. **82**, 789 (2010)
- [16] M. Mézard and G. Parisi, J. Phys. A Math. Gen. **29**, 6515 (1996)
- [17] M. Cardenas, S. Franz, and G. Parisi, J. Phys. A Math. Gen. **31**, 163 (1998)
- [18] W. van Meegen, S. M. Underwood, and P. N. Pusey, Phys. Rev. Lett. **67**, 1586 (1991)
- [19] W. Götze, J. Phys.: Condens. Matter **11**, 1 (1999)
- [20] G. Szamel, Europhys. Lett. **91**, 56004 (2010)
- [21] T. R. Kirkpatrick and P. G. Wolynes, Phys. Rev. A **35**, 3072 (1987)
- [22] G. Biroli and J.-P. Bouchaud, in *The Random First-Order Transition Theory of Glasses: a critical assessment*, John Wiley & Sons, Hoboken, New Jersey (2012)
- [23] D. Coslovich, Phys. Rev. E **83**, 051505 (2011)
- [24] J. P. Hansen and I. R. McDonald, *Theory of simple liquids*, Academic Press, London (1986)
- [25] T. R. Kirkpatrick and D. Thirumalai, Journal of Physics A: Mathematical and General **22**, L149 (1989).
- [26] R. Monasson, Phys. Rev. Lett. **75**, 2847 (1995)
- [27] M. Mézard and G. Parisi, J. Phys.: Condens. Matter **12**, 6655 (2000).
- [28] W. Götze, *Complex dynamics of glass-forming liquids, a mode-coupling theory*, Oxford University Press, Oxford (2009)
- [29] J.-L. Barrat, W. Götze, and A. Latz, J. Phys.: Condens. Matter **1**, 7163 (1989)
- [30] A. Ayadim, P. Germain, and S. Amokrane, Phys. Rev. E **84**, 061502 (2011)
- [31] J. Zinn-Justin, *Quantum field theory and critical phenomena*, Clarendon Press, Oxford (1989)
- [32] T. Temesvári, C. De Dominicis, and I. R. Pimentel, Eur. Phys. J. B **25**, 361 (2002)
- [33] P. Attard, J. Chem. Phys. **93**, 7301 (1990)
- [34] B. Bildstein and G. Kahl, J. Chem. Phys. **100**, 5882 (1994)
- [35] B. Bildstein and G. Kahl, Phys. Rev. E **47**, 1712 (1993)
- [36] A. R. Denton and N. W. Ashcroft, Phys. Rev. A **39**, 426 (1989)
- [37] M. S. Wertheim, Phys. Rev. Lett. **10**, 321 (1963)
- [38] E. Thiele, J. Chem. Phys. **39**, 474 (1963)
- [39] J. K. Percus and G. J. Yevick, Phys. Rev. **110**, 1 (1958)
- [40] F. Caltagirone et al., Phys. Rev. Lett. **108**, 085702 (2012)
- [41] S. Franz, , H. Jacquin, G. Parisi, P. Urbani and F. Zamponi, *to appear in* Proc. Nat. Acad. Sc. (2012)
- [42] S. Franz, , H. Jacquin, G. Parisi, P. Urbani and F. Zamponi, *submitted to* J. Chem. Phys. (2012)
- [43] J.E. Mayer and M. G. Mayer, *Statistical mechanics*, Wiley, New York (1940)
- [44] T. Morita and K. Hiroike, Progr. Theor. Phys. **25**, 537 (1961)
- [45] T. Morita and K. Hiroike, Progr. Theor. Phys. **23**, 385 (1959)
- [46] S. F. Edwards and M. Schwartz, J. Stat. Phys. **110**, 497 (2003)
- [47] B. Kim and K. Kawasaki, J. Phys. A: Math. Gen. **40**, F33 (2007)
- [48] A. Andreanov, J.-P. Bouchaud, and G. Biroli, Europhys. Lett. **88**, 16001 (2009)
- [49] J. Kurchan, G. Parisi, and F. Zamponi, J. Stat. Mech. (2012) P10012
- [50] P. Charbonneau, A. Ikeda, G. Parisi, and F. Zamponi, Proc. Nat. Acad. Sci. **109**, 13939 (2012)